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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

(ATTORNEY'S DOCKET NUMBER

(REV 10-95)

514420-3596

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

(U.S. APPLICATION NO. (if known,

(see 37 C.F.R. 1.5)

09/000330

INTERNATIONAL APPLICATION NO

PCT/JP96/02133

INTERNATIONAL FILING DATE

29 JULY 1996

[EARLIEST] PRIORITY DATE CLAIMED

2 AUGUST 1995

TITLE OF INVENTION

**TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE  
OF HEAT-ROLLER TYPE COPIER**

APPLICANTS FOR DO/EO/US

**Toru NAKAMURA, Toshimi NISHIOKA, Takuya HOGA, Nobuyuki  
KUROKAWA, Junichi FUKUZAWA, Horst-Tore LAND, and Fredy  
HELMER-METZMANN**

Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)), including 0 sheets of formal drawings and a copy of the International Search Report.
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventors (35 U.S.C. 371(c)(4)).
10. ☐ The annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:  
PCT/RO/101 (7 pages)  
PCT/IB/308, 338, 409  
PCT/IPEA/416, 409  
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17. ☒ The following fees are submitted:

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**Basic National Fee (37 CFR 1.492(a)(1)-(5):**

Search Report has been prepared by the EPO or JPO.....\$930.00(\$930.00

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4 Claims /Number Filed / Number Extra /Rate (

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Independent Claims / 1 - 3 = / 0 /X \$82.00 (\$000.00 /

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NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

**WILLIAM F. LAWRENCE  
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745 FIFTH AVENUE  
NEW YORK, NEW YORK 10151**

SIGNATURE

WILLIAM F. LAWRENCE  
NAME

28,029

REGISTRATION NUMBER

Dated: **JANUARY 29, 1998**

#3  
JA  
101 Rec'd PCT/PTO 20 MAY 1998

PATENT  
514420-3596

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Nakamura et al.  
Serial No. : Not Yet Known  
Corresponding Int'l  
Appln. No. : PCT/JP96/02133  
Int'l Filing Date : July 29, 1996  
For : **TONER FOR DEVELOPING ELECTROSTATICALLY  
CHARGED IMAGE OF HEATROLLER TYPE COPIER**  
Examiner: : Not yet known

154-136

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COMMUNICATION

Assistant Commissioner for Patents  
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**ATTENTION: BOX PCT**

Sir:

Attached are the original executed inventor's  
declarations along with Check No. 01729 for 130.00 to cover the

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required surcharge fee. A copy of the specification, as filed, is attached to the declarations since the serial number of the application was not yet available to the inventors when the declaration was signed.

This Communication is being filed without a copy of the Notification of Missing Requirements because that document has not yet been received by applicants' counsel. If such a Notice is mailed by the PTO before this Communication is processed, it is requested that this Communication be considered as responsive to the Notification of Missing Requirement.

Please charge any additional fees required to Deposit Account No. 50-0320.

Respectfully submitted,

FROMMER LAWRENCE & HAUG LLP  
Attorneys for Applicants

By



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Attorney Docket No. 514420-3596

New Patent Application filed **January 29, 1998**, entitled:  
**TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE OF HEAT-  
ROLLER TYPE COPIER,**

corresponding to PCT/JP96/02133  
filed July 29, 1996

Express Mail No.: EM009635902US  
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PATENT  
514420-3596

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Nakamura et al.  
U.S. Serial No. : Not Yet Known  
Corresponding Int'l. App. : PCT/JP96/02133  
International Filing Date : 29 July 1996  
Priority Dates Claimed : 02 August 1995  
For : TONER FOR DEVELOPING  
ELECTROSTATICALLY CHARGED  
IMAGE OF HEAT-ROLLER TYPE  
COPIER

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PRELIMINARY AMENDMENT

Box PCT  
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Sir:

Preliminary to the examination of this U.S.  
national phase application, please enter the following  
amendments:

IN THE CLAIMS:

Claim 3, line 2: delete "or 2"; and

Claim 4, line 2: delete "2 or 3,".

REMARKS

This application includes multiple claim dependencies. The amendment removes the multiple claim dependencies, and the filing fee for this application was computed on the basis that no dependent claim depends from more than one preceding claim.

Entry of this amendment and an early examination on the merits are respectfully solicited.

Respectfully submitted,

FROMMER LAWRENCE & HAUG LLP

Attorneys for Applicants

By



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WFL/erp

TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE OF  
HEAT ROLLER TYPE COPIER OR PRINTER

Technical Field

The present invention relates to a toner for developing an electrostatically charged image of a heat roller type copier or printer. More specifically, this invention relates to a dry one-component magnetic toner, a dry one-component nonmagnetic toner, a dry two-component toner or a liquid toner which, when fixed, is excellent in anti-spent toner effect, and can form a well fixed, highly transparent, sharp image.

Background Art

Heat roller fixing type electrostatically charged image developing copiers and printers are gaining popularity because of widespread office automation. With this background, demand is growing for high grade or sharp copied or printed images which are highly light transmissive and well fixed. General formulations for toners in heat roller fixing type electrostatically charged image developing copiers and printers are shown in Table 1. One of the main factors for improving the sharpness, light transmission and strength of fixing of the image is a binder resin, a chief component of the toner. That is, a heat roller fixing type electrostatically charged image developing copier or printer feeds a toner to an electrostatically charged image on a latent image carrier to obtain a visible image, then transfers the resulting toner image to a plain paper or an OHP film, and fixes the transferred image. Currently, styrene-acrylate resin and polyester resin are widely used as binder resins. With the former resin, however, the light transmission and clarity of the resulting toner are not fully satisfactory, resulting in difficulty in obtaining a high grade image. The latter resin, on the other hand, imparts sufficient



light transmission, but the resin is yellowish in color, thus decreasing clarity.

Table 1

(Unit: wt.%)

	Binder resin	Coloring agent	Charge control agent	Functioning agent	Magnetic powder	Solvent
Dry two component system	50-100	0-20	0-10	0-20	-	-
Dry nonmagnetic one component system	50-100	0-20	0-10	0-20	-	-
Dry magnetic one component system	0-100	0-20	0-10	0-20	0-60	-
Liquid toner	15-50	0-10	0-5	0-10	-	50-70

The present invention has been accomplished in the light of the aforementioned problems. The object of this invention is to provide a toner in a dry two-component toner developer, a dry nonmagnetic one-component toner developer, a dry magnetic one-component toner developer, and a liquid toner developer which toner gives a higher grade copy image, namely, an image excellent in strength of fixing, light transmission and sharpness, in a heat roller fixing type electrostatically charged image developing copier or printer.

#### Disclosure of the Invention

A first aspect of the present invention is to provide a toner for developing an electrostatically charged image of

a heat roller type copier or printer, the toner consisting essentially of a binder resin, a colorant and a charge control agent, wherein the binder resin at least includes a polyolefin resin having a cyclic structure, and a polyolefin resin of a cyclic structure having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, a heat distortion temperature (HDT) by DIN53461-B of 70°C or higher, and a number average molecular weight of 7,500 or more and a weight average molecular weight of 15,000 or more, as measured by GPC, is contained in a proportion of less than 50% by weight based on the entire binder resin.

A second aspect of the invention is to provide the toner for developing an electrostatically charged image according to the first aspect of the invention, in which the binder resin consists of 1 to 100 parts by weight of a polyolefin resin having a cyclic structure, and 0 to 99 parts by weight of at least one resin selected from polyester resins, epoxy resins, polyolefin resins, vinyl acetate resins, vinyl acetate copolymer resins, styrene-acrylate resins, and other acrylate resins.

A third aspect of the invention is to provide the toner for developing an electrostatically charged image according to the first or second aspect of the invention, in which the polyolefin resin having a cyclic structure has at least one functional group selected from a carboxyl group, a hydroxyl group and an amino group.

A fourth aspect of the invention is to provide the toner for developing an electrostatically charged image according to the first, second or third aspect of the invention, in which the polyolefin resin having a cyclic structure is an ionomer, or has a diene-crosslinked structure.

To solve the problems, we, the inventors, have worked out a measure involving the use of a colorless, highly transparent resin. Examples of such a resin are polycarbonates, polyacrylates, polymethacrylates and polystyrenes. These resins, however, are known to be

unsatisfactory in terms of the properties required of binder resins, such as fixing strength and heat response characteristic, and to be questionable when used as binder resins. We have conducted extensive studies to correct these drawbacks, and have found that a toner providing a high grade image can be produced by using a colorless, transparent, highly light transmissive polyolefin resin having a cyclic structure, the polyolefin resin containing less than 50% by weight of a high-viscosity resin based on the entire binder resin. This finding has led us to accomplish the present invention. A toner using as a binder resin a polyolefin resin of a cyclic structure satisfying these characteristics is excellent in fixability, heat response characteristic, and light transmission, achieves a high grade, sharp image, and when used as a color toner, can exhibit its features.

The present invention will now be described in detail.

The toner for developing an electrostatically charged image of a heat roller type copier or printer according to the present invention consists essentially of a binder resin, in which the binder resin at least includes a polyolefin resin having a cyclic structure, and a polyolefin resin of a cyclic structure having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, a heat distortion temperature (HDT) by DIN53461-B of 70°C or higher, and a number average molecular weight of 7,500 or more and a weight average molecular weight of 15,000 or more, as measured by GPC, is contained in a proportion of less than 50% by weight based on the entire binder resin.

The polyolefin resin having a cyclic structure used herein is, for example, a copolymer of an alpha olefin, such as ethylene, propylene or butylene, with an alicyclic compound having a double bond, such as cyclohexene or norbornene, which copolymer is colorless and transparent, and has high light transmittance. This polyolefin having a cyclic structure is a polymer obtained, for instance, by a

polymerization method using a metallocene catalyst or a Ziegler catalyst.

Preferred as the colorless, transparent, highly light-transmissive polyolefin of a cyclic structure used in the present invention are a low-viscosity resin having a number average molecular weight of 1,000 to 7,500, preferably 3,000 to 7,500, and a weight average molecular weight of 1,000 to 15,000, preferably 4,000 to 15,000, as measured by GPC, an intrinsic viscosity (i.v.) of less than 0.25 dl/g, and a heat distortion temperature (HDT) by DIN53461-B of lower than 70°C, and a high-viscosity resin having a number average molecular weight of 7,500 or more, preferably 7,500 to 50,000, and a weight average molecular weight of 15,000 or more, preferably 15,000 to 100,000, as measured by GPC, an i.v. of 0.25 dl/g or more, and an HDT of 70°C or higher.

The low-viscosity polyolefin having a cyclic structure has the above-mentioned number average molecular weight  $M_n$ , weight average molecular weight  $M_w$ , intrinsic viscosity (i.v.) and heat distortion temperature (HDT). The  $M_w/M_n$  ratio, used as a measure of the degree of dispersion of molecular weight distribution, is as small as from 1 to 2.5, namely, a nearly monodisperse state. Thus, a toner having a quick heat response and a high fixing strength, properties required of a toner, can be realised. This polyolefin resin having a cyclic structure according to the present invention is characterized by the following facts: To T745 with a number average molecular weight of 4,000 to be shown later in Table 2, for example, there was added 5% of the azo pigment Permanent Rubin F6B (Hoechst). The mixture was thoroughly dispersed with a kneader, then formed into a sheet by means of a press, and measured for light transmittance using the Macbeth densitometer RD914 (filter SPI red) with visible light of 624 nm. Its light transmittance was 12.0%. Whereas styrene-acrylate resin showed light transmittance of 7.0%, and polyester resin, 15.5%. Hence, the polyolefin resin having a cyclic

structure was confirmed to have high transparency even in a pigment-dispersed system, and to be usable for a color toner as is polyester resin. Measurement by DSC has shown this polyolefin resin to require very low heat of fusion. Thus, this resin can be expected to markedly reduce energy consumption for fixing.

The high-viscosity polyolefin resin having a cyclic structure has the aforesaid properties. Compared with the same resin with a low viscosity, therefore, this resin imparts structural viscosity to the toner, thereby improving offset preventing effect and adhesion to a material to be copied on, such as a paper or film. The low-viscosity polyolefin resin having a cyclic structure, on the other hand, improves the melt flowability of the toner, and satisfies toner characteristics requiring instantaneous melting and solidifying behaviors.

If the amount of the high-viscosity resin used is 50% or more, however, the uniform kneadability of the resin-pigment mixture extremely will decline, deteriorating toner performance. As a result, the toner will become poor in fixability and heat response characteristic, thus resulting in the failure to obtain a high grade, sharp image.

In the present invention, a toner using a binder resin comprising a mixture of other resin with the polyolefin resin having a cyclic structure, which satisfies the foregoing characteristics, also achieves an image of a high grade, i.e., with high fixing strength and sharpness. In this case, it is preferred that the proportions of the polyolefin resin having a cyclic structure and the other resin in the binder resin are to be 1 to 100, preferably 20 to 90, more preferably 50 to 90 parts by weight of the former, and 0 to 99, preferably 10 to 80, more preferably 10 to 50 parts by weight of the latter. If the amount of the former resin is less than 1 part by weight, it becomes difficult to obtain a high grade image.

If a carboxyl group is introduced into the polyolefin

resin having a cyclic structure by the melt air oxidation method or modification with maleic anhydride, its compatibility with the other resin and the dispersability of the pigment can be improved. The same improvement can be achieved by introducing a hydroxyl group or an amino group by a known method.

Furthermore, fixability can be improved by copolymerizing the polyolefin resin having a cyclic structure with a diene monomer such as norbornadiene or cyclohexadiene, or by introducing a crosslinking structure into the polyolefin resin of a cyclic structure, which has a carboxyl group introduced therein, by adding a metal such as zinc, copper or calcium.

The toner for developing an electrostatically charged image of a heat roller type copier or printer according to the present invention can be obtained by adding a colorant, a charge control agent, and if desired, a functioning agent, and other additives to the aforementioned binder resin, and performing known methods such as kneading, grinding and sifting. If desired, a flowing agent may be further added.

The colorant may be a known one, such as carbon black, diazo yellow, phthalocyanine blue, quinacridone, carmine 6B, monoazo red or perylene.

Examples of the charge control agent are known ones such as Nigrosine dyes, fatty acid modified Nigrosine dyes, metallized Nigrosine dyes, metallized fatty acid modified Nigrosine dyes, chromium complexes of 3,5-di-tert-butylsalicylic acid, quaternary ammonium salts, triphenylmethane dyes, and azochromium complexes.

If desired, a known functioning agent, preferably, wax with a melting point of 60 to 170°C, may be added to the toner of the present invention in order to enhance the offset preventing properties during fixing by a heat roller. Examples of the wax with this melting point are carnauba wax, montan wax, and glycerol monostearate.

To the toner of the present invention, there may be

further added a flowing agent such as colloidal silica, aluminum oxide or titanium oxide, and a lubricant comprising a fatty acid metal salt such as barium stearate, calcium stearate or barium laurate.

The toner of the present invention may be used as a toner for one component developers or two component developers. Moreover, the toner of the present invention may be used as a one component magnetic toner by incorporating a magnetic powder, or may be used as a full color toner.

The present invention will be described in more detail by reference to Examples and Comparative Examples.

<Toner preparation method I>

Dry nonmagnetic one component system and dry two component system:

Five % by weight of a charge control agent (Copy Charge NX, Hoechst), 2.5% by weight of wax (Hoechst Wax E, Hoechst), 0.5% by weight of aerosol silica (HDK-H2000, Wacker Chemie), 5% by weight of magenta pigment (Permanent Rubin F6B, Hoechst), and 87% by weight of a binder resin were mixed, and melt kneaded at 130°C by a two roll mill. Then, the mixture was cooled down to solidification, and crushed, followed by powderizing the particles using a jet mill. The resulting fine particles were sieved or sifted to select particles with an average particle diameter of about 10 micrometers, thereby preparing a toner.

<Toner preparation method II>

Dry magnetic one component system:

Forty % by weight of a magnetic powder (BL100, Titanium Industry), 5% by weight of a charge control agent (Copy Charge NX, Hoechst), 2.5% by weight of wax (Hostastat FE-2, Hoechst), 0.5% by weight of aerosol silica (HDK-H2000, Wacker Chemie), 2% by weight of calcium carbonate (Shiraishi Calcium), and 50% by weight of a binder resin were mixed, and melt kneaded at 150°C by a two roll mill. Then, the mixture was cooled down to solidification, and crushed, followed by powderizing the particles using a jet

mill. The resulting fine particles were sifted to select particles with an average particle diameter of about 10 micrometers, thereby preparing a toner.

<Toner preparation method III>

Liquid toner:

Forty % by weight of a mixture consisting of 1 part by weight of carbon black (MA-7, Mitsubishi Kagaku) as a colorant, 0.5 part by weight of a charge control agent (Reflex Blue R51, Hoechst), and 98.5 parts by weight of a binder resin was mixed with 60% by weight of an electrolytic solution (Isopar H, Exxon). The mixture was kneaded with a sand mill to prepare a toner.

Examples 1 to 27 and Comparative Examples 1 to 6

Using the toner preparation methods and binder resins shown in Table 2 below, toners of Examples 1 to 27 and Comparative Examples 1 through 6 were produced. Table 3 presents the fundamental properties of the polyolefin resins having a cyclic structure used, and the trade names of other resins used.

Table 2-1

Ex.No.	Comp. Method of Toner preparation	Formulation of binder resin			
		Sample No.		wt. %	
Ex.					
1	I	1	87	-	-
2	I	1	58	2	29
3	I	1	58	7	29
4	I	3	87	-	-
5	I	3	58	7	29



6	I	5	87	-	-
7	I	5	58	7	29
8	II	1	50	-	-
9	II	1	30	2	20
10	II	1	30	7	20
11	II	1	30	8	20
12	II	3	50	-	-
13	II	3	30	7	20
14	II	3	30	8	20
15	II	5	50	-	-
16	II	5	30	7	20
17	II	5	30	8	20
18	III	1	39.4	-	-
19	III	1	24	2	15.4
20	III	1	24	7	15.4
21	III	1	24	8	15.4
22	III	3	39.4	-	-
23	III	3	24	7	15.4

24	III	3	24	8	15.4
25	III	5	39.4	-	-
26	III	5	24	7	15.4
27	III	5	24	8	15.4
Comp. Ex.					
1	I	7	87	-	-
2	I	8	87	-	-
3	II	7	50	-	-
4	II	8	50	-	-
5	III	7	39.4	-	-
6	III	8	39.4	-	-

Table 3

<u>Sample No.</u>	<u>Product</u>	<u>Mw</u>	<u>Mn</u>	<u>i.v.</u>	<u>HDT</u>	<u>D</u>	<u>Tg</u>
1	T745	7000	3800	0.19	<70	1.8	68
2	S-8007	70000	35000	0.8	$\geq 70$	2.0	80
3	T-745-MO	6800	3400	<0.25	<70	2.0	78
5	T-745-CL	12000	3400	<0.25	<70	3.5	76
7	Tafton NE2155 Polyester resin of Kao Corp.						
8	MC100 Styrene-acrylate resin of Nihon Carbide						

#### <Evaluations>

The toners prepared by the above toner preparation method I or II were each placed in a commercially available electrophotographic copier (PC100, Canon Inc.), and subjected to performance test. Then, the toners prepared

by the toner preparation method III were each placed in a commercially available electrophotographic copier (FT400i, Ricoh Co., Ltd.), and subjected to performance test. The results are shown in Table 4.

Table 4-1

	<u>Fixability</u> <u>10 copies</u> <u>per min</u>	<u>Image sharpness</u>		<u>Light</u> <u>transmission</u> <u>624 nm</u>	<u>Anti-toner</u> <u>spent</u> <u>properties</u>
		<u>Thin line</u> <u>resolving</u> <u>power</u>	<u>Gray</u> <u>scale</u>		
Ex.1	○	○	○	○	○
Ex.2	○	○	○	○	○
Ex.3	○	△	△	△	△
Ex.4	○	○	○	○	○
Ex.5	○	○	○	○	○
Ex.6	○	○	○	○	○
Ex.7	○	△	△	△	△
Ex.8	○	○	○	-	○
Ex.9	○	○	○	-	○
Ex.10	○	○	○	-	△
Ex.11	○	○	○	-	△
Ex.12	○	○	○	-	○
Ex.13	○	○	○	-	○
Ex.14	○	○	○	-	○
Ex.15	○	○	○	-	○
Ex.16	○	○	○	-	△
Ex.17	○	○	○	-	△
Ex.18	○	○	○	-	○
Ex.19	○	○	○	-	○

Ex.20	○	○	○	-	-
Ex.21	○	○	○	-	-
Ex.22	○	○	○	-	-
Ex.23	○	○	○	-	-
Ex.24	○	○	○	-	-
Ex.25	○	○	○	-	-
Ex.26	○	○	○	-	-
Ex.27	○	○	○	-	-
Comp. Ex.1	×	△	△	○	×
Comp. Ex.2	×	×	×	×	×
Comp. Ex.3	×	○	○	-	×
Comp. Ex.4	×	○	○	-	×
Comp. Ex.5	×	○	○	-	×
Comp. Ex.6	×	○	○	-	×

#### Evaluation methods and evaluation criteria

##### 1) Fixability

The toners prepared with the respective formulations were each used for copying onto recycled papers at a copying rate of 10 copies/min at a fixing temperature of 110 to 140°C, with the fixing temperature for each copying cycle being raised by 10°C. The resulting copy samples were rubbed 10 times with an eraser by using an abrasion tester of Southerland. The load during the test was 40 g/cm<sup>2</sup>. The tested samples were measured for the printing density using a Macbeth reflection densitometer. The symbol × was assigned when even one of the measured values at the respective temperatures was less than 65%. The symbol △

was assigned when the measured values at the respective temperatures were 65% or more but less than 75%. The symbol ○ was assigned when the measured values at the respective temperatures were 75% or more.

## 2) Image sharpness

The toners prepared with the respective formulations were each used for copying onto recycled papers. The resulting samples were checked against sample images of Data Quest. The thin line resolving power and gray scale of the copy image were used as bases for evaluation. The symbol × was assigned when the thin line resolving power was 200 dots/inch or less, △ for a thin line resolving power of 201 to 300 dots/inch, and ○ for a thin line resolving power of 301 dots/inch or more. The ratio of the reflection density of the copy image to that of the reflection density of the sample image, at each step of the gray scale, was evaluated as × when less than 65%, △ when 65% or more but less than 75%, and ○ when 75% or more.

## 3) Light transmission

The magenta-colored toners prepared with the formulations of the Examples and the Comparative Examples were each used to produce sheet-shaped samples 100 micrometers thick. The light transmission of each sheet sample was measured using an optical filter having a peak at 624 nm. The light transmittance at 624 nm was evaluated as × when less than 8%, △ when 8% or more but less than 11%, and ○ when 11% or more.

## 4) Anti-toner spent properties

The toner described in each of the Examples and the Comparative Examples and a ferrite carrier of Powdertech were put in predetermined amounts into a developer box. After the mixture was stirred and triboelectrically treated for 1 week, 5 g of the toner-deposited carrier was weighed. This carrier was put in water with soap to remove the toner electrostatically adhering to the surface. Only the carrier magnetic powder was collected using a magnet. The

magnetic powder was immersed in acetone to dissolve and remove the spent toner fused to the surface. A change in the weight after immersion compared with the weight before immersion was evaluated as ○ when less than 0.2%, △ when 0.2 or more but less than 0.5%, and × when 0.5% or more.

The toner for developing an electrostatically charged image of a heat roller type copier or printer according to the present invention contains a binder resin at least including a polyolefin resin having a cyclic structure, in which a high-viscosity polyolefin resin having a cyclic structure is contained in a proportion of less than 50% by weight based on the entire binder resin. Thus, the toner is excellent in fixability, light transmission, and anti-toner spent properties, gives a high quality sharp image, and exhibits its features particularly when used in a color toner.

What is claimed is:

1. A toner for developing an electrostatically charged image of a heat roller type copier or printer, said toner consisting essentially of a binder resin, a colorant and a charge control agent, wherein said binder resin at least includes a polyolefin resin having a cyclic structure, and a polyolefin resin of a cyclic structure having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, a heat distortion temperature (HDT) by DIN53461-B of 70 °C or higher, and a number average molecular weight of 7,500 or more and a weight average molecular weight of 15,000 or more, as measured by GPC, is contained in a proportion of less than 50% by weight based on the entire binder resin.
2. The toner for developing an electrostatically charged image as claimed in claim 1, wherein said binder resin consists of 1 to 100 parts by weight of a polyolefin resin having a cyclic structure, and 0 to 99 parts by weight of at least one resin selected from polyester resins, epoxy resins, polyolefin resins, vinyl acetate resins, vinyl acetate copolymer resins, styrene-acrylate resins, and other acrylate resins.
3. The toner for developing an electrostatically charged image as claimed in claim 1 or 2, wherein said polyolefin resin having a cyclic structure has at least one functional group selected from a carboxyl group, a hydroxyl group and an amino group.
4. The toner for developing an electrostatically charged image as claimed in claim 1, 2 or 3, wherein said polyolefin resin having a cyclic structure has a structure crosslinked by metal ions or dienes.

## Abstract

This invention relates to a toner for developing an electrostatically charged image of a heat roller type copier or printer, the toner consisting essentially of a binder resin, a colorant and a charge control agent, in which the binder resin at least includes a polyolefin resin having a cyclic structure, and a polyolefin resin of a cyclic structure having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, a heat distortion temperature (HDT) by DIN53461-B of 70 °C or higher, and a number average molecular weight of 7,500 or more and a weight average molecular weight of 15,000 or more, as measured by GPC, is contained in a proportion of less than 50% by weight based on the entire binder resin. The toner for developing an electrostatically charged image according to the invention is excellent in fixability, light transmission, and anti-toner spent properties, giving a sharp, high quality image, can be applied to any of a dry one-component magnetic toner, a dry one-component nonmagnetic toner, a dry two-component toner and a liquid toner, and exhibits marked effects particularly when used in a color toner.



DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Under 37 CFR § 1.63, includes reference to PCT International Applications)

FROMMER LAWRENCE & HAUG LLP  
File No.: 514420-3596

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention ENTITLED: *TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE OF HEAT ROLLER TYPE COPIER OR PRINTER*, the specification of which      is attached hereto X was filed on July 29, 1996 as      United States X PCT Application No. PCT/JP96/02133, with amendments through DATE EVEN HEREWITH (if applicable, give details).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT International application(s) designating at least one country other than the United State of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT International applications designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) on which priority is claimed:

Prior Foreign/PCT Application(s) [list additional applications on separate page]:      Priority  
Claimed:

<u>Country (or PCT)</u>	<u>Application Number:</u>	<u>Filed (Month/Day/Year)</u>	<u>Yes</u>	<u>No</u>
PCT	PCT/JP96/02133	JULY 29, 1996	X	
JAPAN	HEI-7(1995)-216751	AUGUST 2, 1995	X	
JAPAN	HEI-7(1995)-354063	DECEMBER 29, 1995	X	

I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. (or U.S.-designating PCT) Application(s) [list additional applications on separate page]:

<u>U.S. Serial</u> <u>No.:</u>	<u>Filed</u> <u>(Month/Day/Year)</u>	<u>PCT Application No.</u>	<u>Status (patented, pending,</u> <u>abandoned)</u>
N/A	N/A	N/A	N/A

I hereby appoint William F. Lawrence, Registration No. 28,029 and Frommer Lawrence & Haug LLP Registration No. 20,999, or their duly appointed associate, my attorneys or agents, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive

DECLARATION FOR PATENT APPLICATION  
AND POWER OF ATTORNEY (Under 37 CFR § 1.63)

FLH Docket No. 514420-3596

the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and specify that all communications about the application are to be directed to the following correspondence address:

WILLIAM F. LAWRENCE, Esq.  
c/o FROMMER LAWRENCE & HAUG LLP  
745 Fifth Avenue  
New York, NY 10151

Direct all telephone calls to:  
(212) 588-0800  
to the attention of:  
WILLIAM F. LAWRENCE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

INVENTOR(S):

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

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Citizenship: Japan

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

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Citizenship: Japan

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Full name of third joint inventor: HOGA Takuya  
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Signature: \_\_\_\_\_ Date: \_\_\_\_\_

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Full name of sixth joint inventor: LAND, Horst-Tore  
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Full name of seventh joint inventor: HELMER-METZMANN, Fredy  
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Citizenship: Germany

NOTE: In order to qualify for reduced fees available to Small Entities, each inventor and any other individual or entity having rights to the invention must also sign an appropriate separate "Verified Statement (Declaration) Claiming for Supporting a Claim by Another for Small Entity Status" form (e.g. for Independent Inventor, Small Business Concern, Nonprofit Organization, Individual Non-Inventor).

the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and specify that all communications about the application are to be directed to the following correspondence address:

WILLIAM F. LAWRENCE, Esq.  
c/o FROMMER LAWRENCE & HAUG LLP  
745 Fifth Avenue  
New York, NY 10151

Direct all telephone calls to:  
(212) 588-0800  
to the attention of:  
WILLIAM F. LAWRENCE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

INVENTOR(S):

Signature: Toru Nakamura Date: May 6, 1998

1-00 Full name of sole or first inventor: NAKAMURA Toru JPX  
Residence: 13-201, Tsukushino 3-Chome, Abiko-shi, Chiba, Japan  
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Signature: T. Nishio Date: Apr. 28, 1998

2-00 Full name of second joint inventor: NISHIOKA Toshimi JPX  
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Citizenship: Japan

Signature: T. Hoge Date: Apr. 28, 1998

3-00 Full name of third joint inventor: HOGA Takuya JPX  
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Signature: A. Kurokawa Date: May 6, 1998

4-00 Full name of fourth joint inventor: KUROKAWA Nobuyuki JPX  
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Citizenship: Japan

Signature: [Signature] Date: Apr. 28 '98

5-00 Full name of fifth joint inventor: FUKUZAWA Junichi JPX  
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Citizenship: Japan

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Full name of sixth joint inventor: LAND, Horst-Tore  
Residence: Am Obertor 30, 65719 Hofheim, Germany  
Citizenship: Germany

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Full name of seventh joint inventor: HELMER-METZMANN, Fredy  
Residence: Stadecker Weg 5, 55270 Essenheim, Germany  
Citizenship: Germany

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NOTE: In order to qualify for reduced fees available to Small Entities, each inventor and any other individual or entity having rights to the invention must also sign an appropriate separate "Verified Statement (Declaration) Claiming [or Supporting a Claim by Another for] Small Entity Status" form [e.g. for Independent Inventor, Small Business Concern, Nonprofit Organization, Individual Non-Inventor]

#3

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Under 37 CFR § 1.01, includes reference to PCT International Application)

FROMMER LAWRENCE & HAUG LLP  
File No.: 514420-3596

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention ENTITLED: TONER FOR DEVELOPING ELECTROSTATICALLY CHARGED IMAGE OF HEAT ROLLER TYPE COPIER OR PRINTER, the specification of which is attached hereto X was filed on July 29, 1996 as United States X PCT Application No. PCT/JP96/02133, with amendments through DATE EVEN HEREWITH (if applicable, give details).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT International application(s) designating at least one country other than the United State of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT International applications designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) on which priority is claimed:

Prior Foreign/PCT Application(s) [list additional applications on separate page]: Priority Claimed:

Country (or PCT)	Application Number:	Filed (Month/Day/Year)	Yes	No
PCT	PCT/JP96/02133	JULY 29, 1996	X	
JAPAN	HEI-7(1995)-216751	AUGUST 2, 1995	X	
JAPAN	HEI-7(1995)-354063	DECEMBER 29, 1995	X	

I hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. (or U.S.-designating PCT) Application(s) [list additional applications on separate page]:

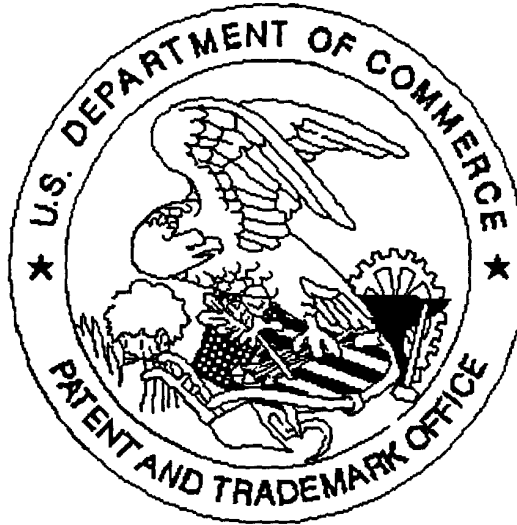
U.S. Serial No.:	Filed (Month/Day/Year)	PCT Application No.	Status (patented, pending, abandoned)
N/A	N/A	N/A	N/A

I hereby appoint William F. Lawrence, Registration No. 28,029 and Frommer Lawrence & Haug LLP Registration No. 20,999, or their duly appointed associate, my attorneys or agents, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive

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